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(54) PROCESS FOR PREPARING CRYSTALLINE SORBITOL IN GRANULAR FORM

(71) We, TOWA KASEI KOGYO CO., LTD., a corporation duly organized under the laws of Japan, and with Post Office address at 2 Otemachi 2-chome, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention for which we pray that a Patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention relates to a process for preparing crystalline sorbitol in granular form.

An object of the invention is to provide an industrial process for preparing crystalline sorbitol in granular form.

Another object of the invention is to provide an improved process for preparing dry crystalline sorbitol.

A further object of the invention is to provide an advantageous process for preparing dry crystalline sorbitol in granular form directly from a so-called molten sorbitol.

Other objects will be apparent from the following description.

Sorbitol is customarily produced in aqueous solution by hydrogenating an aqueous solution of glucose, and it is largely marketed in solution form. For many purposes, however, it is desirable that sorbitol be in dry granular form.

There have been developed various processes for preparing solid sorbitol from aqueous solution or sorbitol. For example, when seed of sorbitol and a suitable organic solvent are added to a concentrated aqueous solution of sorbitol and agitated gently and thereafter the mixture is cooled, crystalline sorbitol of high purity is crystallized out and can be separated from the mother liquor. However, such a process is expensive and time consuming, involving procedures controlled only with difficulty or the use of expensive equipment.

And, when a thickly concentrated aqueous solution of sorbitol containing a minute water content, that is, a so-called molten sorbitol, is cooled as it is, the whole thereof solidifies in an amorphous and transparent glassy form. This solid has not been found to be practical because it can not form crystalline granules or powder even when said solid is smashed or pulverized.

On the contrary, when seed of powdery or granular sorbitol amounting to about 3—30% of solid matter of a molten sorbitol is added to said molten sorbitol and the resultant mixture is agitated at a predetermined temperature and thereafter agitation is stopped and the mixture is cooled, the whole of the mixture solidifies into a mass in which plenty of small crystals grow and stick to each other. Said mass of solid sorbitol can be smashed or pulverized into crystalline sorbitol in granular or powdery form, which is allotted now for all the industrial uses of solid sorbitol, even though it has a purity slightly lower than that of the crystalline sorbitol prepared by the aforementioned process where solvents are used. However, the customary process above-mentioned is accompanied with a large disadvantage that it takes some dozen hours to cool and solidify the whole of the mixture.

An improvement of the above-mentioned process for preparing granular or powdery sorbitol has been proposed, in which a molten sorbitol is sprayed upon the surface of a large quantity of sorbitol seed agitated previously in an operation tank and the mixture is thereafter cooled to obtain crystalline sorbitol in granular form immediately. However, there has been an industrial disadvantage in this process in that a large amount of sorbitol seed in comparison with that of the molten sorbitol to be sprayed, for example, five to seven times as much as the amount of the molten sorbitol, has to be provided continuously. Moreover, there are unfavourable points in that the molten sorbitol sticks to the inner wall of the operation tank and molten adhesion among formed granules themselves takes place frequently in said process.

We have investigated to remove many disadvantages of the conventional processes and found that, when the mixture of seed and

molten sorbitol prepared as in the conventional process is agitated consecutively under suitable conditions of temperature and water content thereof, plenty of small crystals grown in the mixture do not stick to each other and the whole of the mixture can be converted into a soft and plastic mass, and consequently such a soft and plastic mass can be moulded into granules immediately by using appropriate apparatus. The surface area of the soft and plastic mass prepared as in the above is increased so remarkably by moulding said mass into granular form immediately that the succeeding procedures, that is, cooling and drying of the solid sorbitol can be accomplished in an extremely short time. Crystalline sorbitol in powdery form can be prepared readily by pulverising the above granular sorbitol.

The present invention provides a process for preparing crystalline sorbitol in granular form which comprises agitating molten sorbitol having a water content below 15%, adding sorbitol seed amounting to 1—50% of the solid matter of the molten sorbitol to said molten sorbitol so as to reduce the water content of the resultant mixture below 10%, agitating said mixture at a temperature between 60°C and 96°C to convert the whole of the mixture into a state of soft plasticity containing plenty of small crystals, sending the above plastic mixture to an extrusion moulding machine and extruding it into vermicelli-form cooling the resulted mouldings in vermicelli-form to a temperature below 60°C and thereafter cutting them into a predetermined length.

The invention will be further described in detail with the drawing which shows the relation between temperature and water content necessary for making the plastic state of the mixture consisting of seed and molten sorbitol.

According to the present invention a molten sorbitol prepared by concentrating an aqueous solution of sorbitol down to a water content less than 15% is poured continuously into an appropriate agitation apparatus, for example, a kneader, while adding continuously seed of granular or powdery sorbitol amounting to 1—50% of the solid matter of the poured molten sorbitol to said molten sorbitol so as to reduce the water content of the resultant mixture below 10%, and moreover agitation or kneading of the mixture is continued at a predetermined temperature. Said mixture is thus in a liquid state at first, however, plenty of small crystals grow and ripen gradually and the whole of the mixture becomes a soft and plastic mass. The suitable temperature, at which the mixture shows such a soft and plastic state, lies between 60°C and 96°C, and suitable water content of the mixture is below 10% as described above. That is, the viscosity of said mixture increases with drop of temperature or decrease of water content thereof, and the agitating or kneading of the mixture becomes impossible when the viscosity thereof is increased by too much, while the plastic state of the mixture can not be obtained because of viscosity decrease at a temperature above 96°C or at a water content above 10% of the mixture.

The amount of seed to be added to the molten sorbitol should be increased or decreased in direct proportion to temperature and water content of said molten sorbitol. The maximum amount (50%) of seed is added when water content of the molten sorbitol is 15%. The most industrially advantageous amount of seed to be added in the present process is about 10% of the solid matter of the molten sorbitol, and the optimum time of agitation or kneading lies between about 5 minutes and 20 minutes.

The figure shows the above relation between temperature and water content in the rectangular co-ordinates graduating the water content on the X-axis and temperature on the Y-axis respectively. That is, such a mixture having temperature and water content indicated by each point in the area drawn with oblique lines in the figure shows the soft plasticity under the condition that the mixture is agitated or kneaded. And the most favourable temperature and water content of the mixture for industrial embodiment of the invention is indicated by each point on the line B and its neighbouring area. The above-mentioned meaning of the figure can be expressed with concrete values of temperature and water content of the mixture as in the following Tables I and II.

Table I

Temperature	Scope of water content
60°C	0—10%
70°C	0—6.7%
80°C	0—3.9%
90°C	0—1.4%
96°C	0%

Table II

Scope of Temperature	Scope of water content
60—70°C	0—10%
70—80°C	0—6.7%
80—90°C	0—3.9%
90—96°C	0—1.4%

And moreover, the lines A and B in the above figure can be expressed with following mathematical formulas in said rectangular co-ordinates.

line A: $y=10^{1.98227-0.02035x}$ (1)

line B: $y=10^{1.53983-0.11897x}+47.6$ (2)

In other words, the aforementioned area drawn with oblique lines in the figure is surrounded with three lines expressed mathe-

matically by the above formula (1), y=60 and x=0 respectively, in the rectangular co-ordinates. And the most favourable conditions in the invention are indicated by each point on the line expressed mathematically by the above formula (2) (y>60) and its neighbouring area in the rectangular co-ordinates.

When the formation of small crystals in the mixture has progressed sufficiently and the whole of the mixture has been converted into a soft and plastic mass containing plenty of small crystals as described above, said plastic mass is sent continuously to an appropriate moulding machine, for example, a moulding machine of screw-extrusion type and extruded in vermicelli-form from the discharging end of said machine. These extruded mouldings have surface areas several ten times to several hundred times as wide as that of the original plastic mass containing small crystals, and therefore the moulded sorbitol in vermicelli-form is rapidly cooled and dried while further growth of the crystals therein is promoted at the same time. It is desirable that the solid sorbitol of vermicelli-form has diameter of 1—3mm and length of 200—500mm. The sorbitol of vermicelli-form cooled to a temperature below 60°C is then cut and formed into predetermined length by means of a suitable grain-regulating machine, for example, flash mill.

In the invention, the novel phenomenon that the mixture of molten sorbitol and seen can be converted into the state of soft plasticity, is grounded on the physico-chemical property of sorbitol to crystallize out with difficulty from its aqueous solution in comparison with glucose and other sugars. In other words, the invention is intended to prepare granular sorbitol immediately from molten sorbitol by applying the physico-chemical property of sorbitol to crystallize out with difficulty.

According to the process of the invention the crystalline sorbitol in granular form can be obtained continuously and in a very short time compared with the conventional processes. And granules or powder of sorbitol prepared according to the process of the invention has many advantages, that is, higher melting point, low hygroscopic and adhesive properties, excellent fluidity and facilities of packing and preserving.

The following examples illustrate several embodiments of the process of the invention.

EXAMPLE 1

An aqueous solution of sorbitol having a purity of about 99.5% was concentrated in vacuo at a temperature of 120°C to reduce the water content thereof to a value below 1%, and the obtained molten sorbitol was cooled to a temperature of about 90°C. Said molten sorbitol was poured into a continuous kneader at a rate of 1 kg per minute, while adding powdery sorbitol seed at a rate of 0.1 kg per minute to the poured molten sorbitol, and the resultant mixture was agitated at a temperature of 70—80°C for about 10 minutes to cause to grow and ripen plenty of small crystals. A soft plastic mass was obtained, and this plastic mass was sent continuously to a moulding machine of screw-extrusion type, from which said mass was extruded into vermicelli-form having diameter of 2mm and length of 300—500mm. After cooling the mouldings in vermicelli-form to a temperature of about 40°C, said mouldings were cut onto a suitable length by means of a flash mill. Granular sorbitol obtained was a crystalline solid having water content below 1% and melting point of 96.0—97.5°C.

EXAMPLE 2

An aqueous solution of sorbitol having about 99.0% was concentrated in vacuo to reduce the water content thereof to a value below 1% and the obtained molten sorbitol was cooled to a temperature of about 80°C. This molten sorbitol was poured into a continuous kneader at a rate of 1 kg per minute, while adding powdery sorbitol seed at a rate of 0.05kg per minute to the poured molten sorbitol, and the resultant mixture was agitated at a temperature of 70—80°C for about 15 minutes to cause to grow and ripen plenty of small crystals. A soft and plastic mass thus obtained was treated in the same way as described in Example 1 and granules of crystalline sorbitol having water content below 1% and melting point of 96.0—97.2°C were obtained.

EXAMPLE 3

An aqueous solution of sorbitol having a purity of about 97.0% was concentrated in vacuo to reduce the water content thereof to about 10% and the obtained molten sorbitol was cooled to a temperature of about 70°C. This molten sorbitol was poured into a continuous kneader at a rate of 1 kg per minute, while adding powdery sorbitol seed at a rate of 0.3 kg per minute to the poured molten sorbitol, and the resultant mixture was agitated at a temperature of 60—70°C for about 15 minutes to cause to grow and ripen plenty of small crystals. A soft and plastic mass thus obtained was treated in the same way as described in Example 1 except the moulding in vermicelli-form was dried for 30 minutes by using hot wind with a temperature of 70—80°C and thereafter was cooled to a temperature of about 40°C. Granular sorbitol obtained was crystalline solids having water content below 1% and melting point of 94.0—96.0°C.

EXAMPLE 4

An aqueous solution of sorbitol having a

purity of about 97.0% was concentrated in vacuo to reduce the water content thereof to about 13% and the obtained molten sorbitol was cooled to a temperature of about 70°C. Said molten sorbitol was poured into a continuous kneader at a rate of 1kg per minute, while adding a powdery sorbitol seed at a rate of 0.5kg per minute to the poured molten sorbitol, and the resultant mixture was agitated at a temperature of 60—70°C for about 12 minutes to cause to grow and ripen plenty of small crystals. A soft and plastic mass thus obtained was treated in the same way as described in Example 3 and crystalline sorbitol in granular form having water content below 1% and melting point of 94.0—95.5°C was obtained.

WHAT WE CLAIM IS:—

1. A process for preparing crystalline sorbitol in granular form which comprises: agitating molten sorbitol having a water content below 15%, adding sorbitol seed amounting to 1—50% of the solid matter of the molten sorbitol to said molten sorbitol so as to reduce the water content of the resultant mixture below 10%, agitating said mixture at a temperature between 60°C and 96°C to convert the whole of the mixture into a state of soft plasticity containing plenty of small crystals, sending the above plastic mixture to an extrusion moulding machine and extruding it into vermicelli-form, cooling the resulted mouldings in vermicelli-form to a temperature below 60°C and thereafter cutting them into a predetermined length.

2. A process as defined in claim 1 in which temperature and water content of the mixture are between 60°C and 70°C and below 10%, respectively.

3. A process as defined in claim 1 in which temperature and water content of the mixture are between 70°C and 80°C and below 6.7%, respectively.

4. A process as defined in claim 1 in which temperature and water content of the mixture are between 80°C and 90°C and below 3.9%, respectively.

5. A process as defined in claim 1 in which temperature and water content of the mixture are between 90°C and 96°C and below 1.4%, respectively.

6. A process as defined in claim 1 in which agitating or kneading of the mixture is continuously carried out by means of using a kneader apparatus.

7. A process as defined in claim 6 in which agitating or kneading in the kneader apparatus is carried out for about 5—20 minutes.

8. A process as defined in claim 1 in which a moulding machine of screw-extrusion type is used as moulding machine.

9. A process as defined in claim 8 in which sorbitol of vermicelli-form has diameter of 1—3mm and length of 200—500mm.

10. A process as defined in claim 8 in which a flash mill is used for cutting solid sorbitol of vermicelli-form.

11. A process for preparing crystalline sorbitol in granular form substantially as herein before described and illustrated with reference to the accompanying drawings.

12. Crystalline sorbitol in granular form whenever prepared by a process as claimed in any one of the preceding claims.

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1287509 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*